Advanced Global Atmospheric Gases Experiment (AGAGE)

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INTRODUCTION

The Advanced Global Atmospheric Gases Experiment (AGAGE) and its predecessors provide continuous high-frequency gas chromatographic measurements of biogenic and anthropogenic gases that are carried out at globally distributed sites in order to quantitatively determine the source and sink strengths and circulation of a large number of chemically and radiatively important long-lived gases. The program that started in 1978 is conveniently divided into three parts associated with three changes in instrumentation: the Atmospheric Lifetime Experiment (ALE), the Global Atmospheric Gases Experiment (GAGE), and AGAGE. Beginning in 1978, these three successive automated, high-frequency, in situ experiments have documented the long-term behavior of the measured concentrations of these important gases over the past 23 years and show both the evolution of latitudinal gradients and the high-frequency variability due to sources and circulation.

AGAGE began over the 1993-1996 time period and continues to the present. It has two instrument components. First, a highly improved gas chromatographic system measures five biogenic/anthropogenic gases (CH_4, N_2O, $CHCl_3$, CO, and H_2) and five anthropogenic gases (CCl_3F, CCl_2F_2, CH_3CCl_3, CCl_2FCClF_2, and CCl_4). Each species is measured 36 times per day with an electron capture detector (ECD), flame ionization detector (FID), and mercuric oxide reduction detector (MRD; this detector is for CO and H_2 and is currently present at only two of the stations, Mace Head, Ireland, and Cape Grim, Tasmania). Second, a gas chromatograph-mass spectrometer (GC-MS) system measures a wide range of hydrochlorofluorocarbons and hydrofluorocarbons: CH_2FCF_3 (HFC-134a), CH_3CCl_2F (HCFC-141b), CH_3CClF_2 (HCFC-142b), etc. These are now serving as interim or permanent alternatives to the chlorofluorocarbons and other long-lived halocarbons regulated by the Montreal Protocol [*UNEP*, 1996]. Also measured with the GC-MS system are the methyl halides (CH_3Cl, CH_3Br, and CH_3I) and the halons ($CBrF_3$ and $CBrClF_2$). AGAGE also includes development and use of new, much more accurate absolute calibrations for most of the measured gases.

The ALE, GAGE, and AGAGE stations have been located in five globally distributed localities: (1) Ireland, first at Adrigole, 52°N, 10°W (1978-1983), then at Mace Head, 53°N, 10°W (1987-present); (2) U.S. West Coast, first at Cape Meares, Oregon, 45°N, 124°W (1979-1989), then at Trinidad Head, California, 41°N, 124°W (1995-present); (3) Ragged Point, Barbados, 13°N, 59°W (1978-present); (4) Cape Matatula, American Samoa, 14°S, 171°W (1978-present); (5) Cape Grim, Tasmania, 41°S, 145°E (1978-present).

Of special significance is the AGAGE operation at Samoa. It enables a direct intercomparison with similar real-time measurements (and also with flask measurements) by the CMDL group. This intercomparison has already aided us in determining the net effect of calibration and instrument differences on the measurements by each group so that the data from both the AGAGE and CMDL networks can be utilized in combination by theoreticians to investigate chemical and meteorological phenomena.

RECENT PROGRESS

The instrumentation and calibrations used in the ALE, GAGE, and AGAGE experiments and a history of the majority of the anthropogenic ozone-depleting and climate-forcing gases in air based on these experiments have been described in detail [*Prinn et al.*, 2000]. We provide estimates of the long-term trends in total chlorine contained in long-lived halocarbons involved in ozone depletion. We summarize interpretations of these measurements using inverse methods to determine trace gas lifetimes and emissions. Finally, we provide a combined observational and modeled reconstruction of the evolution of chlorocarbons by latitude in the atmosphere over the past 60 years, which can be used as boundary conditions for interpreting trapped air in glaciers and oceanic measurements of chlorocarbon tracers of the deep oceanic circulation [*Prinn et al*., 2000; see also *Walker et al*., 2000].

A recent analysis of the entire 1978-2000 ALE-GAGE-AGAGE CH_3CCl_3 data set indicates that OH levels in the southern hemisphere are higher than in the northern hemisphere and that OH levels rose between 1978 and 1988,

and then subsequently decreased in 2000 to levels below 1978 values [*Prinn et al.*, 2001]. The 1994-1998 AGAGE $CHCl_3$ measurements have been analyzed, showing that this gas has a pronounced seasonal cycle (driven largely by OH), a global average baseline mole fraction of 8.9 ppt with no significant trend, and a global lifetime of 6.3 months. Inverse methods indicate emissions are predominantly in the 30°N-90°N region [*O'Doherty et al.*, 2001]. *Miller* [1998] established the abundance and trends of $CHClF_2$ and CH_3Br. *Huang* [1999] produced new estimates of OH using CH_3CCl_3, $CHClF_2$, CH_2FCF_3, CH_3CCl_2F, and CH_3CClF_2, simultaneously. An analysis of the GAGE-AGAGE measurements of CH_4 for 1985-1999 indicates a decreasing trend, in agreement with previous independent analyses, and has yielded estimates of CH_4 emissions in each semi-hemisphere [*Cunnold et al.*, 2002]. Measurements of CH_3Br from AGAGE and other investigators have been modeled with the 3D Model of Atmospheric Transport and Chemistry (MATCH) [*Jensen*, 1999]. A comprehensive discussion of the use of Kalman filters in trace gas inverse problems has been published [*Prinn*, 2000]. A critical analysis of polynomial-based approaches to the CH_3CCl_3 inverse problem has also been published [*Prinn and Huang*, 2001].

AGAGE GC-MRD measurements of hydrogen at Cape Grim have been reported and interpreted [*Simmonds et al.*, 2000]. GAGE/AGAGE measurements of CCl_3F indicate its global concentrations reached a maximum in 1993 and decayed slightly after that, while CCl_2F_2 levels continued to increase, but only slowly since 1993 [*Cunnold et al.*, 1997; *Prinn et al.*, 2000]. Several AGAGE scientists were lead authors or co-authors in the 1998 ozone assessment [*Kurylo et al.*, 1999; *Prinn et al.*, 1999]. Analysis of regional pollution events in Ireland suggest that industry estimates of the rate of decline in European emissions are too small [*Derwent et al.*, 1998a]. Measurements of CCl_4 from July 1978 to June 1995 show a maximum in its global concentration in 1990, followed by a small decrease since then [*Simmonds et al.*, 1998a]. GC-MS measurements of CH_2FCF_3, CH_3CCl_2F, and CH_3CClF_2 at Mace Head indicate rapid increases in the levels of these CFC replacements, and that industry estimates of HCFC-141b and particularly HCFC-142b emissions appear far too small to explain the observations [*Simmonds et al.*, 1998b]. Measurements of $CHClF_2$ (HCFC-22) in the Cape Grim archive and at La Jolla have been used to estimate OH concentrations, and this yields values larger than those determined from CH_3CCl_3 (but because of the larger uncertainty in the HCFC-22-based estimate, the difference is not statistically significant) [*Miller et al.*, 1998].

A Lagrangian dispersion model has been used to analyze 1996 Mace Head observations showing that North American sources occasionally produce pollution events at this station, which are about 10% of those due to the European sources [*Ryall et al.*, 1998]. Mace Head data for CH_4, N_2O, and CO_2 have been analyzed to elucidate European and northern-hemispheric sources [*Derwent et al.*, 1998b]. *Wamsley et al.* [1998] reported measurements of the halon $CBrClF_2$. *Fraser et al.* [1999] discussed halon trends and emissions over the past 20 years. *Fraser and Prather* [1999] reviewed the current prognosis for recovery of the ozone layer. D.S. Cohan, et al. (Methyl iodide observations at Cape Grim, Tasmania, using the AGAGE GC-MS instrument, submitted to *Journal of Atmospheric Chemistry*, 2002) reported AGAGE CH_3I measurements at Cape Grim and interpreted them using trajectory analysis. *Dunse et al.* [2001] reported the results of modeling studies of Cape Grim pollution episodes recorded in AGAGE measurements.

The ALE/GAGE/AGAGE data are available through the Department of Energy-Carbon Dioxide Information Analysis Center (DOE-CDIAC) World Data Center (e-mail to cpd@ornl.gov, Dataset No. DB-1001).

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